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Analytical Capabilities of RIMS: Absolute Sensitivity and Isotopic Analysis

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1. Introduction

Resonance ionization mass spectrometry (RIMS) with thermal filament sources is rapidly becoming an established analytical technique. Research at Los Alamos National Laboratory (Miller et al. 1982; Miller and Nogar 1983a&b; Downey et al. 1984a&b); Oak Ridge National Laboratory (Donohue and Young 1983; Donohue et al. 1983, 1984a&b; Young and Donohue 1983; Young et al. 1984), and the National Bureau of Standards (Fassett et al. 1983a&b, 1984) has demonstrated the utility of RIMS in isotope ratio measurements for a wide variety of elements and mixtures of elements. Advantages of RIMS over conventional thermal ionization mass spectrometry in isotope ratio measurement include the reduction or elimination of isobaric interferences and potentially greater sensitivity and dynamic range. Reduction of isobaric interferences is an almost automatic consequence of RIMS, since the excitation process makes use of electronic resonances which are characteristic of a particular element. Sensitivity is a consequence of the efficiency of the ionization process (Hurst et al. 1979) and the reduction of interfering signals. Potential increases in dynamic range may also result from the ability to ionize with isotopic selectivity, thus reducing the tailing from dominant mass peaks into the detection channel for minor isotopes.

We will present in this paper the results of recent isotope ratio measurements carried out on small (60-200 ng) lutetium samples. The sensitivity and selectivity of continuous wave (cw) laser RIMS allow the accurate determination of very large ratios ($\sim 10^6$) in real samples containing numerous isobaric interferences. In addition, high resolution optical spectra of lutetium isotopes have been generated using RIMS as a prelude to isotopically selective resonance ionization.

We will also present the results of two-color spectroscopic studies for future isotope ratio measurements in technetium. A large number of multiply-resonant sequences have been explored; however, the presence of Tc molecular species appears to limit the potential sensitivity of the measurement.

2. Experimental

Analytical measurements on lutetium were carried out using the magnetic sector mass spectrometer and broadband cw dye laser system described previously (Miller and Nogar 1983b). Major isotopes were measured using current detection, while pulse counting was necessary for minor isotopes. Approximately eight minutes of signal integration was used for the former, while on the order of 25 minutes was required for the latter. Backgrounds resulting

from scatter from major isotopes and residual thermal ionization were subtracted in pulse counting for minor isotopes; corrections were typically thirty percent.

High resolution optical spectra were obtained using the magnetic mass spectrometer with an actively stabilized ring dye laser. This narrowband laser source provided close to the same ionization efficiency as the broadband case, with ample resolution (<1 MHz) to distinguish hyperfine structure, to the extent allowed by Doppler- and power-broadened linewidths. The isotopic resolution provided by the mass spectrometer permitted the collection of interference-free spectra for even low-abundance isotopes.

Multicolor resonance ionization of technetium was performed using two dye lasers pumped by a single, pulsed excimer laser, with time-of-flight mass spectrometer detection (Downey et al. 1984b). The laser outputs, ~ 1 -4 mJ each, were counterpropagated through the source region after equal optical path lengths. Ions were detected by a channel electron multiplier connected to a gated integrator. Optical spectra were obtained by scanning of the appropriate laser.

3. Results and Discussion

3.1 Lutetium Analyses and Spectroscopy

In previous work, we have demonstrated the selective one-color, two photon ionization of lutetium via the $452\text{ nm } ^2D_{3/2}(5d6s^2)+^2D_{3/2}(5d6s6p)$ resonance (Miller et al. 1982). We subsequently showed (Miller and Nogar 1983b) a greatly enhanced ion yield using cw laser excitation, and suggested the use of this apparatus for chemical analysis. We report here on the determination of a sample containing a mixture of rare earth isotopes, predominately Lu and Yb. Typical sample aliquots contained ~ 60 -200 ng of Lu, primarily the naturally occurring isotopes ^{175}Lu and ^{176}Lu .

Table 1 shows the results of Lu isotope ratio determination for both RIMS and conventional thermal ionization. The effect of isobaric interferences in the 173 and 174 mass positions is obvious, despite extensive chemical cleanup of the sample. Internal precision in the RIMS measurements is also good, being 16, 4, and 2 percent for the three ratios, respectively. Note that for ^{173}Lu , this represents a determination with a total of as few as 10^8 atoms (2.7×10^{-14} g). Confirmation of the results for ^{173}Lu and ^{174}Lu was provided by mass separation and radioactive decay counting, a process of several days duration, to an agreement of about one percent. Ionization efficiency in these measurements was also found to be relatively high, with the ratio of ions collected to atoms loaded being 10^{-4} .

Table 1. Isotope Ratio Measurements

	RIMS	Thermal
173/175	4.4×10^{-7}	3.36×10^{-3}
174/175	3.62×10^{-6}	9.28×10^{-4}
176/175	2.64×10^{-2}	2.63×10^{-2}

It has been suggested (Miller and Nogar 1983a&b) that single frequency (linewidth <1 MHz) laser excitation may lead to an increase in both sensitivity and selectivity. Improvement in the former stems from a better match of

the excitation and absorption linewidths, thus allowing saturation of the resonant transition. Selectivity should also be improved since the narrower linewidth should decrease the probability of accidental coincidence with interfering species. Isotopically selective ionization may also be possible, allowing measurement of larger ratios through a reduction in mass tailing from the dominant isotope.

In order to carry out isotopically selective RIMS, it is necessary to understand in detail the spectroscopic behavior of the analyte, a difficult task for very rare or unstable isotopes. We have initiated a spectroscopic study (Miller et al. 1984) of rare lutetium isotopes using the single mode ring dye laser system described above. Figure 1 shows a sample spectrum obtained for ^{176}Lu obtained at reduced intensity, $I=300\text{ W/cm}^2$, to minimize power broadening. At least six of the ten possible hyperfine components are clearly resolved, and a comparison with similar data obtained (Miller et al. 1984) for ^{175}Lu shows considerably broader hyperfine structure for ^{176}Lu . This suggests that a significant degree of selectivity favoring ^{176}Lu may be possible in the resonance ionization process. As mentioned earlier, selective ionization of minor isotopes can lead to a significant improvement in available dynamic range.

Spectra were also obtained for ^{174}Lu and ^{173}Lu using samples similar to those described above, demonstrating the potential to acquire high-resolution optical spectra of rare isotopes without extensive isotope enrichment through the combination of single-frequency laser excitation and highly mass-resolved ion detection. This capability will enable us to measure isotope shifts and hyperfine structure of optical transitions of these isotopes and thereby obtain important nuclear parameters such as nuclear spin, nuclear quadrupole moment, and nuclear spin coupling constants--quantities of fundamental importance to nuclear theorists.

3.2 Technetium Spectroscopy

The high ionization potential of technetium, 7.28 eV, presents a problem for cw resonance ionization. For the simplest ionization scheme, two-photon single-color ionization, lasers operating in the ultraviolet region of the spectrum must be used in order to have sufficient energy to cross the ionization barrier. With current technology, the ultraviolet region can only be accessed with rather modest power. An alternative method, doubly-resonant three-photon ionization relieves the wavelength restriction but requires the use of two lasers overlapped in space (and time if pulsed lasers are used).

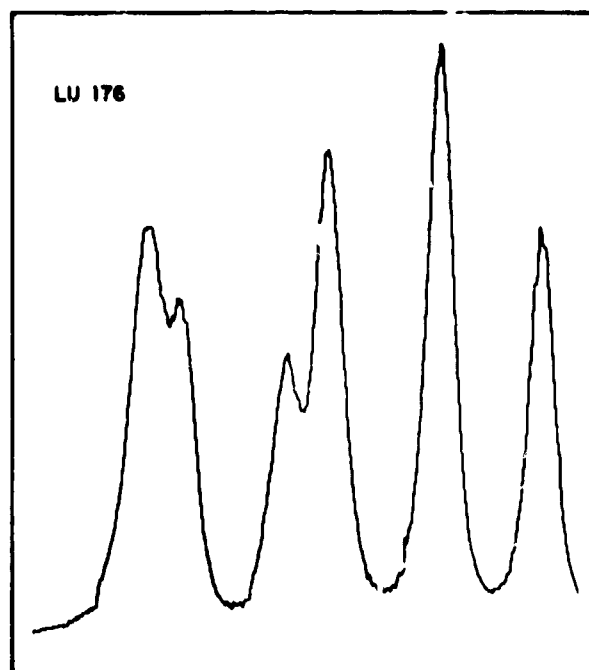
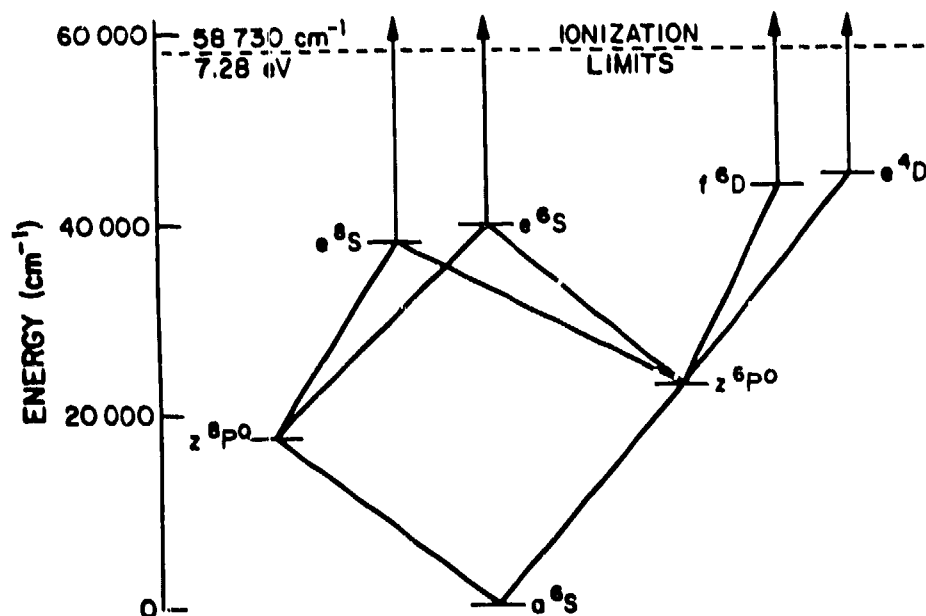


Fig. 1. Optical spectrum of ^{176}Lu obtained using RIMS showing hyperfine structure of the $2D_{3/2} - 2D'_{3/2}$ transition.

Early last year, we conducted a number of experiments on the two photon, ultraviolet resonance ionization of Tc (Nogar et al. 1983). Calculations carried out at that time suggested that pulsed ionization using available laser sources (repetition rate ~ 10 Hz @ 1 mJ in the ultraviolet) would not provide sensitivity sufficient to detect the anticipated (Cowan and Haxton 1980) 10^7 - 10^8 Tc atoms with reasonable accuracy, although selectivity was adequate to discriminate against molybdenum isobaric interferences. Since our recent findings (Miller and Nogar 1983 a&b) suggest better sensitivity using cw lasers, we have investigated resonance ionization schemes at wavelengths where cw lasers could eventually be used.

The generalized photoionization schemes used in this work involve two resonant absorptions followed by ionization from the second intermediate, Figure 2. The f^6D and e^4D manifolds were reached from the ground state by sequential absorption of two blue photons, $\lambda_1 \sim 420$ nm and $\lambda_2 \sim 460$ nm. Ionization from these levels could be effected by photons of either color. The e^8S and e^6S manifolds were reached by, respectively: $\lambda_1 \sim 610$, $\lambda_2 \sim 420$ nm, and $\lambda_1 \sim 420$ nm, $\lambda_2 \sim 600$ nm. Ionization from these manifolds can only be carried out by the more energetic photons. Twenty-six unique three-photon ionization sequences are allowed for these resonant intermediates from the ground state by $\Delta L = \pm 1$ and $\Delta J = 0, \pm 1$ selection rules in Tc. We have observed twenty-two of these schemes; the remaining four were not attempted experimentally. In addition, we have observed considerable optical structure between atomic resonances. This structure is attributed (Downey et al. 1984b) to the production of technetium ions from a molecular precursor. Results were qualitatively similar for a variety of sample preparation methods and filament materials. In terms of selectivity, it appears that three-photon ionization of technetium will be the best RIMS scheme for molybdenum-bearing samples. Free Mo has no known visible electronic transitions originating from the ground state. The potential for photoionizing Mo is much reduced, as compared with two-photon, ultraviolet ionization (Nogar et al. 1983).



Recent calculations (Downey et al. 1984b), together with experimental results in other systems, suggest that one may expect $>10^{-5}$ conversion of Tc atoms leaving a sample filament to detectable ions. This is based on a 5% geometrical overlap of sample with the laser beam (Keller and Nogar 1984), 50% population of the ground state of Tc, and a calculated 10^{-3} efficiency for conversion of irradiated ground state atoms to ions. Samples containing $>10^8$ atoms would thus be amenable to cw RIMS analysis if 100% of the sample evaporates as atoms. The experiments mentioned above suggest that a considerable fraction of the Tc may evaporate in a molecular form thus greatly reducing the sensitivity and possibly, selectivity.

4. Conclusions

The cw laser RIMS approach has been demonstrated to accurately measure large Lu isotope ratios and detect small levels of minor isotopes even in the presence of isobaric interferences. The same approach can also be used to obtain high resolution optical spectra of rare isotopes. For elements with higher ionization potentials (e.g., Tc), multicolor ionization schemes are necessary for cw RIMS measurements. Two-color RIMS spectra of Tc using pulsed lasers illustrate the feasibility of this approach. For any element, the sensitivity and selectivity of RIMS can be limited by the efficiency of ground state atom production in the sample volatilization step.

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